

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN AND RELATING TO CATALYTIC STRUCTURES HAVING METALLIC SUBSTRATES

(71) We, JOHNSON, MATTHEY & CO., LIMITED, a British Company, of 78, Hatton Garden, London, EC1P 1AE, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to catalysts and to catalytic structures comprising a substrate, an intermediate oxide layer and a catalytic layer which may be used for a wide variety of catalytic reactions, e.g. the catalytic oxidation of ammonia in the manufacture of nitric acid and the catalytic oxidation of organic compounds (e.g. methane, ethane and propylene) for heating purposes and of other carbon containing compounds such as carbon monoxide and for catalytic reduction, e.g. the catalytic reduction of oxides of nitrogen with a reducing fuel and for use in automobile exhaust control units.

The catalysts of the invention may also be used in NOX Abatement units adapted to be attached to plants for the manufacture of nitric acid. Many nitric acid plants use high pressure processes in which the oxidation of ammonia is carried out in the presence of solid rhodium-platinum wire which has been woven into a gauze. It is also highly advantageous to recover from the tail gas plant, energy which can be utilised to supply power to the system. In some systems sufficient energy can be recovered for the process to be self-sustaining and even to provide additional power. This is normally carried out as a catalytic process in which the oxides of nitrogen are reacted with a gaseous reducing fuel. It is important that the catalyst used be highly active, exhibit a minimum resistance to gas flow and catalyse the reaction at low initial reaction or ignition temperatures. The catalyst itself, should however still have reasonably high (e.g. 750–800°C) temperature stability. It is an object of the present invention to provide improved catalysts and catalytic structures for their processes which are alternative to the ones now in use.

Air pollution control by catalytic combustion imposes a number of restrictions on the type of catalyst which may be used. In addition to a requirement that the catalyst should be active at low temperatures, it should be stable under both oxidising and reducing conditions. Further, when the catalyst is packed into a reactor it should have a very low pressure drop across the bed and it should be resistant to attrition, thermal and mechanical shock and clogging by dust particles.

According to the present invention there is provided a catalyst comprising:

- (a) an extended metal substrate made from a heat and oxidation resistant alloy of iron including at least one of the elements chromium (3–40) wt.%, aluminium (1–10) wt.%, cobalt (0–5) wt.%, nickel (0–72) wt.% and carbon (0–0.5) wt.%;
 (b) a first layer on the extended metal substrate and comprising an adherent coating selected from refractory oxides and compounds containing an oxygen containing anion; and
 (c) catalytic material carried by the first layer, the catalytic material

comprising one or more metal selected from ruthenium, rhodium, palladium, iridium, platinum, silver, gold, and alloys containing at least 10% by weight of one of the said metals bismuth antimony or one or more base metal.

5 Conveniently not more than 10 wt.% and preferably not more than 3 or 5 wt.% of the alloy of iron consists of one or more of the additional elements silicon, manganese, zirconium, copper, tungsten, vanadium, molybdenum, cerium, niobium, tantalum and titanium.

10 The oxygen in the first layer may be present as an oxide selected from alumina, silica, titania, zirconia, hafnia, thoria, beryllia, magnesia, calcium oxide, strontium oxide, barium oxide, chromia, boron, scandium oxide, yttrium oxide, and oxides of the lanthanides. Alternatively, the oxygen in the first layer is present as an oxygen containing anion selected from the group consisting of chromate, phosphate, silicate and nitrate.

15 The base metal included in the catalytic material may be aluminium, magnesium, chromium, molybdenum, tungsten, manganese, iron, rhodium, cobalt, titanium, vanadium, copper, zinc, cadmium, indium, tin, lead, a lanthanide or an actinide.

20 One particular group catalysts according to the present invention comprises an extended metal substrate containing 3-40 wt.% chromium, 1-10 wt.% aluminium, a trace to 3 wt.% of one or more of the additional elements and balance, apart from impurities iron.

25 According to another aspect of the invention there is provided a catalyst comprising an extended metal substrate made from a heat resistant alloy having an aggregate nickel and/or chromium content of greater than 20 wt.%, the said heat resistant alloy having relatively high mechanical strength and thermal conductivity, a first layer on the extended metal substrate and comprising an adherent coating containing oxygen and a second layer applied to the first layer and comprising a metal selected from the group consisting of ruthenium, rhodium, palladium, iridium, platinum, silver, gold, an alloy containing at least one of the said metals and alloys containing at least 10 wt.% of one of the said metals.

30 The catalytic material comprising one or more of the platinum group metals listed above or an alloy containing at least one of the said platinum group metals is preferably deposited upon the oxide coating or film and it may be deposited in a form which possesses catalytic activity or which is capable of being rendered catalytically active by subsequent treatment. Catalytic structures according to the present invention are extremely robust and effective in carrying out the hereinbefore defined objects of the invention under the stated reaction conditions.

35 Moreover, we have found that in some reaction environments, e.g. automobile exhaust purification, a metal substrate causes the catalyst to reach running temperature much more quickly and therefore considerably more efficiently than conventional catalysts, e.g. those having a ceramic substrate.

40 In this specification the term "extended metal substrate" means a metallic substrate which has been mechanically deformed in such a way that when compared with a plain non-deformed substrate of the same superficial area, a very much increased surface area is obtained. Typically the increased surface area may be achieved by corrugating or folding in a former and winding up a flat foil and a corrugated foil together into a tube having a spiral cross section.

45 In a preferred embodiment of the present invention, the metallic substrate which is employed in the catalytic structure is first crimped, corrugated, folded, indented and/or perforated in such a way that a very much extended surface area is produced. Such a surface area is normally much greater than that obtained with ceramic honeycombs or with particulate catalyst supports for the same given volume. An example of a metallic substrate made in accordance with this invention and comprising a roll of corrugated sheet of a heat resisting alloy interleaved with a non-corrugated sheet of such alloy. Alternatively, two corrugated sheets may be used with the corrugations in each sheet parallel with each other or at an angle to each other. A coated substrate is then provided with a firmly adherent oxide coating which is porous and absorbent and has a high surface area and which acts as the carrier for the second catalytically active layer containing one or more of the platinum group metals as herein defined.

50 The heat resistant alloys comprising the extended metal substrate are preferably alloys having a minimum nickel plus chromium content of 20% by weight. Typical alloys which therefore may be used for the extended metal substrate are high nickel and chromium stainless steels and proprietary products such as "INCONEL" (Registered Trade Mark) 600 and "INCONEL" 601.

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We prefer to provide the metallic substrate with the first firmly adherent oxide layer in an essentially two stage process. In the stage the metallic substrate is thermally oxidised to provide a thin first oxide layer which acts as a key. We prefer to carry out thermal oxidation by maintaining the formed metallic substrate at from 1000—1200°C in air or moist cracked ammonia vapour for 1 hour. The higher temperature is required with very oxidation resistant alloys such as the Kanthal Registered Trade Mark range and the moist hydrogen atmosphere is preferred with alloys having a high Ni content.

In the second stage the adherent oxygen-containing or oxide film may be produced by any one of several known methods including chemical techniques. The film must be of sufficient thickness to provide adequate absorptive capacity for retaining the catalytically active alloy comprising one or more of the platinum group metals. The film is preferably from 0.004 to 0.001 inches thick.

Where aluminum is present in the alloy forming the extended metal substrate the oxide film may be produced by treating the aluminium-containing surface with a solution of an alkaline carbonate, usually a sodium carbonate chromate solution. The film may be produced by the anodic oxidation of the metal surface whereby the metal is made the anode in an electrolytic solution. In anodising aluminium containing surfaces, a 15 wt.% sulphuric acid solution is commonly employed as the electrolyte but other acid electrolytes such as chromic acid, oxalic acid, phosphoric acid and sometimes boric acid may be used. The oxide film to which this invention relates is deliberately positioned and does not include the relatively thin natural oxide films which sometimes occur on metal surfaces which have been exposed to the atmosphere.

One method of forming an alumina layer on these alloys which do not contain sufficient aluminium to form their own alumina layer upon oxidation is the use of Calorising (Registered Trade Mark). This involves the vapour deposition of an aluminium coating followed by anodising or heating in an oxygen-containing gas. Alternative coatings such as a chromate, a phosphate, silica or silicate or zirconia may all be deposited by known methods. The many different techniques for the preparation of a high surface area catalytically active refractory metal oxide wash coat containing one or more of the refractory metal oxides which confer beneficial properties as regard ageing and inertness to platinum group metals at high temperature under oxidising and reducing conditions are well known in the art and in the interests of brevity need not be reproduced here.

A preferred adherent oxide coating deposited upon the extended metal substrate is alumina.

One method for the deposition of hydrous alumina is proposed in United States Patent No: 2406420. Any convenient aluminium compound such as alkali metal aluminates and aluminium salts may be used as the starting material. Either acidic or basic precipitants are used, depending upon the character of the starting material. Suitable acidic precipitants are ammonium chloride, ammonium sulphate, ammonium nitrate, hydrochloric acid and nitric acid. Suitable basic precipitants are ammonium hydroxide, sodium hydroxide and hexamethylene-tetramine.

One method is to precipitate the hydrous alumina from an alkali metal aluminate solution containing excess aluminium and alkali metal hydroxide directly on to the extended metal substrates forming part of the present invention. If the aluminate solution is maintained at a temperature of 60°—85°C a film or coating of alpha alumina trihydrate (Gibbsite) is deposited. Subsequent heating at 150—180°C converts the trihydrate to the monohydrate and subsequent heating at 540°C converts the monohydrate to gamma alumina without loss of the very high surface area coating which is produced by this method. The high surface area results from the formation of hexagonal crystal aggregates of approximate size $8 \times 8 \times 20$ microns. Micropores of size of 40 Å diameter are present in the hexagonal crystal aggregates but appear to play no part in the catalytic activity of the structure. The high surface area is demonstrated (in Example 12) by resistance to lead and phosphorus poisoning after deposition of catalytic metal.

The heat-and-oxidation resistant alloys comprising the extended metal substrate of the present invention comprise alloys of iron, chromium and aluminium in which the elements cobalt, nickel and carbon are preferably also present. Ranges, apart from trace elements and impurities, for each element which may be present in the alloy are as follows:

		%	—	w/w	
	Cr	3	—	30	
	Al	1	—	10	
	C	0	—	0.5	
5	Co	0	—	5.0	5
	Ni	0	—	15.0	
	Fe	Balance			

Preferred ranges for the above mentioned elements are:

		%	—	w/w	
10	Cr	13	—	24	10
	Al	3.5	—	6.5	
	C	0	—	0.1	
	Co	0.2	—	0.2	
	Ni	0	—	5.0	
15	Fe	Balance			15

Typical quantities of trace elements which may be present in the alloy to improve strength, oxidation-resistance and heat-resistance are:

		%	—	w/w	
	Si	0.2	—	0.9	
20	Mn	0.2	—	0.7	20
	Zr	0.01	—	0.20	
	Cu	0.01	—	0.15	
	Nb	0.01	—	0.3	
	Ta	0.8	—	1.2	
25	Ti	0.8	—	1.2	25
	Ce	0.01	—	1.0	
	Ca	0.01	—	0.5	
	C	0.01	—	0.1	

Specific heat-and-oxidation-resistant alloys suitable for use in carrying out the present invention are given in the following examples:—

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EXAMPLE 1.

Kanthal D (Registered Trade Mark): a proprietary product supplied by the Kanthal Company of Sweden:

30

5		1,492,929	5
		% w/w	
	C	0.09	
	Cr	22.60	
	Co	2.0	
5	Al	4.5	5
	Fe	Balance	

EXAMPLE 2.
Megapyr (Registered Trade Mark): supplied by Telcon Metals Ltd.

		% w/w	
10	Cr	30	10
	Fe	65	
	Al	5	

EXAMPLE 3.
Stainless Steel 316 (one of the standard range of austenitic stainless steels):

15		% w/w	15
	C	0.08	
	Cr	18.00	
	Ni	10.00	
	Ti	0.40	
20	Fe	Balance	20

EXAMPLE 4.
The following range of alloys is supplied by the Kanthal Company of Sweden:

		%	w/w	
	Cr	10	— 40	
25	Al	1	— 9	25
	Fe	51	— 88.9	
	Ta	0.1	— 5	
	Ce	0.01	— 1	

30 In the above composition Ta may be partially replaced by Ti, and Ce may be partially replaced by Ca.
30 Optionally the following constituents may be present to improve the mechanical strength and oxidation resistance of the alloys:

		%	w/w
	Mn	0	— 2
	Si	0	— 2
	C	0	— 0.5
5	Co	0	— 5
	Nb	0	— 2
	Mo	0	— 1.5
	Th	0	— 0.2
	Zr	0.01	— 1, and

10 P and S may be present as impurities.
Examples in this range are as follows:

10

(i)

	%	w/w
	20	— 30
	3.5	— 6
15	Ta	2.5
	Ce	0.15
	Fe	Balance

15

(ii)

	%	w/w
	20	— 30
20	Al	3.5 — 6
	(or Al	2.5)
	Ta	0.1
	Ce	0.1
	Co	0.1 — 5
25	Fe	Balance

20

25

(iii)

	%	w/w
	3.5	— 4
	Al	5 — 9
	Nb	1.5
30	Zr	0.15
	Ta	0.1 — 5
	Fe	Balance

30

(iv)		%	w/w	
	Cr	10	—	15
	Al	3	—	5.5
	Mo	1		
5	Th	0.1		5
	Ta	0.1	—	5
	Ce	0.01	—	1
	Fe	Balance		

EXAMPLE 5.

10 Immaculate 5 (Registered Trade Mark); a proprietary product supplied by 10
Firth Vickers Ltd.

		%	w/w	
	Cr	23.0		
	Ni	21.0		
15	C	0.1		15
	Fe	Balance		

EXAMPLE 6.

20 Inconel 600 (Registered Trade Mark); a proprietary product supplied by 20
Henry Wiggin Ltd.

		%	w/w	
	Ni not less than —	72.00		
	C not more than —	0.15		
	Mn not more than —	1.00		
	Fe	8.00		
25	S not more than —	0.015		25
	Si not more than —	0.50		
	Cu not more than —	0.50		
	Cr	15.50		

Inconel 601

		%	w/w	
30	Ni	60.50		30
	Cr	23.00		
	Fe	14.10		
	Al	1.35		
35	Mn not more than —	0.50		35
	Cu not more than —	0.25		
	Si not more than —	0.25		
	C not more than —	0.50		
	S not more than —	0.007		

EXAMPLE 7.

Inconley 800 (Registered Trade Mark); a proprietary product supplied by Henry Wiggins Ltd.

		%	w/w	
5	Ni	32.50		5
	C not more than —	0.10		
	Mn not more than —	1.50		
	S not more than —	0.15		
	Cu not more than —	0.75		
10	Cr not more than —	21.00		10
	Fe	Balance		

EXAMPLE 8.

Stainless Steel No: 309

		%	w/w	
15	Cr	22 — 24		15
	Ni	12 — 15		
	C not more than —	0.2		
	Mn not more than —	2.0		
	Si not more than —	1.0		
20	Fe	Balance		20

EXAMPLE 9.

Stainless Steel No: 310 (Supplied by the British Steel Corporation)

		%	w/w	
	Cr	24 — 26	(preferably 25)	
25	Ni	10 — 22	(„ 20)	25
	C not more than —	0.25	(„ 0.1)	
	Mn not more than —	2.0	(„ 1.8)	
	Si not more than —	2.0	(„ 1.5)	
	Fe	Balance	Balance	

EXAMPLE 10.

Stainless Steel No: 321

		%	w/w	
	Cr	17	— 19	
5	Ni	9	— 12	5
	C		0.8	
	Mn not more than —		2.0	
	Si not more than —		1.0	
	Ti not less than —		0.4	
10	Fe		Balance	10

EXAMPLE 11.

Armco 18SR supplied by the Armco Corporation

		%	w/w	
	Cr		18	
15	Al		2	15
	Ti		0.4	
	Si		1	
	C		0.05	
	Fe		Balance	

20 Generally speaking, in the Fe—Cr—Al system, there are very few ferrite steels having less than 12—12.5% by weight Cr which are satisfactory. Also the aluminium content for alloys which function satisfactorily is rarely outside the range 1—6% by weight. 20

25 The metal substrate of the present invention is deformed so as to present a large surface area to the vapour phase reactants whose reaction is to be catalysed. This may be carried out, for example, by first producing the alloy in thin sheet form by rolling, corrugating by passage through fluted forming rolls, spirally winding the thin corrugated sheet so that a round sieve-like body is formed, the openings of which correspond to the depths of the grooves in the said corrugated sheet. The two sheets may be wound simultaneously, one of the sheets being corrugated and the other plain, corrugated to a different configuration when compared with the first mentioned corrugated sheet or with the corrugations of the sheets having the same or a different corrugation configuration and with the corrugations in the respective sheets disposed at angles to each other. Where a flat and a corrugated sheet in strip form is used, the leading edges thereof are spot-welded together and strips of a certain length are fed into a device which rolls the strips between three sprung rollers to form a spirally wound collar-like or generally annular-shaped module. 30

35 Extended metal substrates of the present invention possess $1\frac{1}{2}$ —3 times the surface to volume ratio that can be obtained with a ceramic honeycomb substrate. The normal ceramic substrate is 600—700 sq. ft. per cubic foot of substrate. Examples are proprietary products EX 20 (Corning) which has a surface area of 576 sq.ft/ft³ and Grace 400 which is 780 sq.ft/ft³. This is the highest obtained so far and should be compared with 1100 sq. ft/ft³ for 0.003" thick Kanthal D sheet and 2000 sq.ft/ft³ for 0.002 thick Kanthal D sheet. 40

45 We prefer to use foil of thickness between 0.0015 and 0.0045 inch and more preferably of thickness 0.002 inch corrugated and assembled to form a structure having approximately 400 cells per square inch when considered in cross section. 45

A preferred range of cell sizes is 200—800 cells per square inch. Suitable surface to volume ratios are 1200 sq. ft per cubic foot with 400 cells per sq. inch and 2000 sq. ft per cubic foot with 800 cells per square inch.

5 An alternative method of forming the module comprises spot-welding the two strips of foil to a stainless steel tube of, for example, $\frac{1}{4}$ inch outside diameter, which aids winding and module formation. 5

10 In yet another method, the two strips of foil to be simultaneously wound are spot-welded together along their leading edges and then wound upon a hollow conical former, thereafter using friction rollers and slides in the cone, the strip is wound up and is forced into a retaining collar or shell in one operation. 10

15 Where a retaining collar or shell is not used it is desirable to weld successive convolutions of the module by forming one or more radially extending runs of weld on the ends of the module. Other methods of securing successive convolutions or at least the outermost convolutions by stitching or tack-welding may be employed in order to prevent the spirally wound modules from unwinding. 15

After forming the modules into finished units they are preferably cleaned before the formation of the adherent oxygen containing film or coating, and this is preferably carried out by a vapour degreasing technique with a halogen containing solvent such as trichloroethylene followed by washing in acetone and drying.

20

EXAMPLE 12.

20 In this example Gibbsite was deposited on thermally oxidised Kanthal D modules made by winding simultaneously two sheets, of which one is corrugated and the other plain to form a generally cylindrical module. The deposit was obtained by contacting the module with sodium aluminate solution containing excess aluminium and caustic soda at 80°C. After firing the washcoat was found to be almost pure gamma alumina. The washcoat was metallised with a 7½ wt.% Rh/Pt alloy using known techniques to give a metal loading of 30 g/ft³ of volume of the whole catalyst structure. Such structures have been found to have better poison resistance than washcoated ceramics and unwashcoated metallic substrates. This is demonstrated by results obtained from simulated lead and phosphorus trials on catalyst structures with metal and ceramic substrates: 20

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(a) Simulated lead poisoning trials

The test of exhaust gas contained:

35

Hydrocarbons	1000 ppm	
Co	2.5% ppm	
NOX	1000 ppm	
Pb	0.5 gm/hr	balance N ₂

35

Washcoat:	Gamma alumina
Metallised with:	7½ wt.% Rh/Pt

40

Substrate	Washcoat loading g/in ³	Metal loading g/ft ³	Hydrocarbon after 1 hour	conversion 3 hours	efficiency 7 hours
Kanthal D	3.17	30	79%	69%	52%
Kanthal D	1.48	30	74%	63%	56%
45 Kanthal D	0.7	30	67%	48%	36%
Ceramic Ex 20 (Corning) (range of results)	2.0	30	56—75	40—54	27—39

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(b) *Simulated phosphorus poisoning trials*

Washcoat:
Metallised with: Gamma alumina
7½ wt.% Rh/Pt

	Substrate	Washcoat loading g/in ³	Metal loading g/ft ³	Hydrocarbon after 1 hour	conversion 3 hours	efficiency 7 hours	
5	Kanthal D	2.5	30	.98%	97.5%	97%	5
	Kanthal D	1.8	30	96.5%	95.0%	93%	
10	Ceramic Ex 20 (Corning)	2.0	30	85%	76.5%	59	10

Instead of Pb, the test exhaust gas contained 1000 ppm in P in the form of 1% tributylphosphate/toluene in air having a space velocity of 100,000 hr⁻¹.

15 We prefer a washcoat loading which is within the range of 5—30% by weight of the metallic monolith substrate. A suitable loading of Al₂O₃ on Kanthal D having 400 cells per square inch is 10% by weight. The surface area of the alumina is 50—500 square metres per gram of alumina. The aluminate method of deposition of alumina, described above, gives a surface area of from 120—160 square metres per gram of alumina.

20 An alternative preferred method for the deposition of an adherent alumina washcoat on the metallic substrate is to prepare a slurry of a pre-activated Gibbsite (alumina trihydrate) and an alumina monohydrate having a solid-liquid ratio of between 25 and 50 wt.% and a pH less than 7 and using this to impregnate the shaped substrate by complete immersion. The exact strength of the slurry used (which may be determined by trial and error) should be sufficient to produce an alumina washcoat of the required thickness. The substrate is then allowed to dry in warm air and finally fired for 2 hours at 450°C to form chi and gamma alumina in adherent coating up to 0.002 in. thick on the metallic substrate. Crystal aggregates of diameter 3—7 microns are produced having micropores of approximately the same size, i.e. 40 Å in diameter.

30 A further alternative method of deposition of an adherent alumina washcoat on the metallic substrate is to use a slurry of alpha alumina monohydrate. After firing at 450°C gamma alumina is formed having a surface area between 180 and 300 square metres per gram. Gamma alumina is added to alpha alumina monohydrate at the slurring stage before firing in order to form a thixotropic mixture. Crystallite or crystal aggregates of 20—100 Å diameter are formed. Micropore diameters remain the same at 40 Å.

40 Suitable proprietary alumina trihydrates (Gibbsite) are "FRF 80" supplied by British Aluminium Chemicals Ltd. and "C 333" supplied by Conoco (Registered Trade Mark). Suitable alumina monohydrates (Boehmite) are "Sol-Gel Alumina" supplied by the United Kingdom Atomic Energy Authority. "Dispal M" supplied by Conoco and "Condea F" supplied by the Condea Group. Gibbsite is added to "Sol-Gel alumina" (which is microcrystalline Boehmite) at the slurring stage in order to form a thixotropic mixture.

45 Optionally one or more of the oxides titania, zirconia, hafnia and thoria may be present in the alumina for the purpose of providing additional stabilisation of the intermediate oxide (washcoat) layer as described in our British patent No. 1401002. If desired, rare earth oxides, alkaline earth oxides and alkali metal oxides may be used.

50 Many of the aluminium-containing metallic substrates according to the present invention have the property of oxidising "inwards". That is to say we believe that a factor contributory to the success of the present invention is the fact that the extended metal substrate itself, which forms part of the catalytic structure of the present invention has a tendency to oxidise under very strongly oxidising conditions in such a way that the first layer of adherent oxide film does not tend to grow over or cover the outermost layer of alloy-containing platinum group metal, silver or gold.

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Impregnation or deposition of the alloy of platinum group metals, silver or gold and optionally base metal upon the first oxygen containing adherent layer may be accomplished by known methods of deposition of catalytically active metals on washcoats or other supports, e.g. if a high surface area refractory metal oxide is the adherent oxygen containing film, the support may be immersed in a solution of water soluble inorganic salt or salts of platinum group metal, e.g. platinum, rhodium and nickel. In this case chloroplatinic acid, rhodium trichloride and nickel chloride would be used.

We prefer the composition of the outermost layer of catalytic metal to consist of platinum group metals or alloys of the platinum group metals with each other and with base metals. Particularly preferred combinations are 7½% Rh/Pt for automobile exhaust oxidation catalysts, 10% Rh/Pt for oxidation of ammonia and 20–50% Rh/Pt for NOX abatement, i.e. reduction of oxides of nitrogen with a gaseous reducing fuel in nitric acid tail gas purification.

Particularly preferred alloys of platinum, rhodium and base metal which in the present invention are suitable in the outermost catalytic metal alloy layer of the catalyst structure are alloys containing:

		%		w/w	
	Rh	1	—	50	
20	Base Metal	0.01	—	25	20
	Pt			Balance	

in which the base metal is selected from the group consisting of Al, Mg, Cr, Mo, W, Mn, Fe, Co, Ni, Ti, V, Cu, Zn, Cd, Hg, In, Tl, Sn, Pb, the lanthanides and the actinides. This combination is useful for the oxidation and reduction reactions and also in the steam reforming of naphtha and haphtha distillates.

The base metals mentioned above, however, are also useful in other platinum group metal alloy combinations and also, when employing catalytic structures according to the present invention in which the outermost catalytic metal layer contains silver or gold. Ruthenium is useful for the decomposition of NOX in automobile exhaust purification.

EXAMPLE 13.

A three inch wide piece of Kanthal D three thousandths of an in. thick had fifty thousandths corrugations formed in it by the method described above and was formed into a spiral module. It was oxidised for one hour at 1200°C to form an alumina layer adherent upon the substrate. A 7½ wt.% rhodium platinum alloy was then deposited upon the alumina and the catalytic structure was subjected to oxidation trials using a space velocity of an automobile engine exhaust of 80,000 hours⁻¹. The initial hydrocarbon conversion was 73%, after 100 hours it was 66%. The initial light off was 265°C., after 100 hours it was 320°C.

EXAMPLE 14.

A corrugated spiral module formed as described above from a one inch piece of 321 stainless steel was "Calorised" to form an aluminium coating which was then oxidised for one hour at 1000°C and a loading of 25 grams per cubic foot of 7½ wt.% rhodium platinum was placed on the oxide coated substrate. Using a space velocity of 240,000 hours⁻¹ the following results were obtained:

Initial hydrocarbon conversion was 72%, after 24 hours 77%; initial light off 230°C; after 24 hours 290°C.

EXAMPLE 15.

A one inch piece of 316 stainless steel was "Calorised" and oxidised for one hour at 1200°C, using the same loading of rhodium platinum alloy and space velocity as described in Example 14 the following results were obtained:

Initial hydrocarbon conversion was 76%, after initial light off at 195°C; after 24 hours light off was at 290°C.

EXAMPLE 16.

Using foil 0.002" thick made of (a) stainless steel 310 supplied by the British Steel Corporation and (b) Kanthal D supplied by the Kanthal Company of Sweden two cylindrical modules were made up 3" long, 2" in diameter having 800 cells per

square inch (cross section). A high surface area alumina washcoat was deposited on both by the aluminate method described above and 40 gm/cu ft platinum was described upon the alumina by known techniques.

Both units were then engine tested using low-lead fuel according to specification of the Environmental Protection Agency of the United States.

Hydrocarbon
Conversion

Carbon Monoxide
Conversion

Kanthal D (100 hours)

90.8%

99.2%

310 SS (200 hours)

79.4%

90.3%

EXAMPLE 17.

In this example a ceramic monolith is compared with a Kanthal D module both of which have a high loading FRF 80/Sol Gel Alumina washcoat with a 100% Pt catalytic layer and also included is a Kanthal D module having a high loading hydrolytic alumina (aluminate method) washcoating and also having a 100% Pt catalytic layer.

	Washcoat	Dimensions	Effective frontal area	Effective vol.
Ceramic	FRF 80/Sol Gel Al ₂ O ₃	4" x 6"	11.1 sq. in.	66.4 cu. in.
Kanthal D	" " " "	" "	10.75 " "	64.7 " "
Kanthal D	Hydrolytic (Aluminate)	" "	11.4 " "	66.5 " "

Results

The results are sum weighted for automobile engine operation under different conditions:

	Hydrocarbon conversion				Carbon monoxide conversion			
	0 hrs	100 hrs	200 hrs	300 hrs	0 hrs	100 hrs	200 hrs	300 hrs
Ceramic + FRF 80/Sol Gel	92.9	76.6	77.0	75.1	96.1	89.7	94.6	98.2
Kanthal D + FRF 80/Sol Gel	87.8	71.8	75.3	63.0	88.5	90.5	79.5	80.0
Kanthal D + Hydrolytic alumina	92.3	79.3	80.2	75.0	95.4	87.6	91.1	90.0

These results show good comparability of metal supports with ceramic substrates both as regards performance and stability.

WHAT WE CLAIM IS:—

1. A catalyst comprising:

(a) an extended metal substrate made from a heat and oxidation resistant alloy of iron including 3—40 wt % chromium, 1—10 wt % aluminium, 0—5 wt % cobalt, 0—72 wt % nickel and 0—0.5 wt % carbon, balance essentially comprising iron;

(b) a first layer on the extended metal substrate comprising an adherent coating selected from refractory oxides and compounds containing an oxygen-containing anion; and

(c) a catalytic material carried by the first layer, the catalytic material comprising one or more metals selected from ruthenium, rhodium, palladium, iridium, platinum, silver, gold, and alloys containing at least 10% by weight of one of the said metals and bismuth, antimony or one or more base metals.

2. A catalyst according to Claim 1 in which not more than 10% by weight of the alloy of iron consists of one or more of the additional elements silicon, manganese, zirconium, copper, tungsten, vanadium, molybdenum, cerium, niobium, tantalum and titanium.
- 5 3. The catalyst according to Claim 2 in which not more than 5% by weight of the alloy of iron consists of one or more of the said additional elements.
4. A catalyst according to Claim 3 in which not more than 3% by weight of the alloy of iron consists of one or more of the said additional elements.
- 10 5. A catalyst according to Claim 1 in which the first layer is a refractory oxide comprising alumina, silica, titania, zirconia, hafnia, chromia, boria, scandium oxide, yttrium oxide or an oxide of a lanthanide.
6. A catalyst according to any one of Claims 1 to 5 in which the first layer comprises an oxygen-containing anion which is a chromate, phosphate, silicate or a nitrate.
- 15 7. A catalyst according to any one of Claims 1 to 6 in which the catalytic material is a combination of platinum and rhodium.
8. A catalyst according to any one of Claims 1 to 7 in which the said base metal is present and is selected from Al, Mg, Cr, Mo, W, Mn, Fe, Re, Co, Ti, V, Cu, Zn, Cd, In, Sn, Pb, the lanthanides and the actinides.
- 20 9. A catalyst according to Claim 1 in which the base metal is present in an amount from a trace to 25% by weight.
10. A catalyst according to Claim 5 in which the refractory oxide is gamma-alumina.
- 25 11. A catalyst according to Claim 10 in which the gamma-alumina is present as hexagonal crystal aggregates.
12. A catalyst according to Claim 11 in which the hexagonal crystal aggregates are of the approximate size $8 \times 8 \times 20$ microns.
- 30 13. A catalyst according to Claim 10 in which the quantity of alumina deposited upon the metallic substrate is within the range 5—30% by weight of the weight of metallic substrate used.
14. A catalyst according to Claim 13 in which the quantity of alumina deposited upon the metallic substrate is approximately 10% by weight of the weight of metallic substrate used.
- 35 15. A catalyst according to Claim 10 in which the surface area of the alumina as deposited upon the metal substrate is within the range 50—500 square metres per gram of alumina.
16. A catalyst according to Claim 15 in which the surface area of the alumina as deposited upon the metal substrate is within the range 120—160 square metres per gram of alumina.
- 40 17. A catalyst according to Claim 5 in which the refractory oxide is a mixture of chi- and gamma-alumina.
18. A catalyst according to Claim 17 in which the mixture of chi and gamma alumina is present in crystal aggregates of diameter within the range 3—7 microns.
- 45 19. A catalyst according to Claim 5 in which the refractory oxide comprises alumina mixed with one or more of the oxides titania, zirconia, hafnia and thoria.
20. A catalyst according to Claim 5 in which the refractory oxide selected comprises alumina mixed with one or more of the rare earth oxides, the alkaline earth oxides and the alkali metal oxides.
- 50 21. A catalyst according to any preceding claim wherein the extended metal substrate is made from a heat resistant alloy having an aggregate nickel and/or chromium content greater than 20 wt. %.
22. A process for the manufacture of nitric acid by the oxidation of ammonia in which there is used a catalyst according to any previous claim.
- 55 23. A process for the chemical reduction of an oxide of nitrogen with a gaseous reducing fuel in the presence of a catalyst according to any of Claims 1 to 21.
24. A process for the purification of an automobile exhaust gas using a catalyst as claimed in any one of Claims 1 to 21.
- 60 25. A process for the oxidation of hydrocarbons or carbon monoxide using a catalyst as claimed in any one of Claims 1 to 21.
26. A process according to Claim 22 in which the process is ammonia oxidation and a combination of Rh and Pt containing approximately 10% by weight Rh is used as the catalytic material.
27. A process according to Claim 23 in which the process is reduction of an

oxide of nitrogen and a combination of rhodium and platinum containing 20—50% by weight Rh is used as the catalytic material.

28. A process according to Claim 24 in which the process is purification of an automobile exhaust gas and a combination of rhodium and platinum containing approximately 7½% by weight Rh is used as the catalytic material.

29. A process according to Claim 25 in which the process is oxidation of hydrocarbons or carbon monoxide and a combination of rhodium and platinum containing approximately 7½% by weight Rh is used as the catalytic material.

30. A process according to any one of Claims 22—25 in which the catalytic material has a composition within the range:

	% w/w
Rh	1 —50
Base metal	0.01—25
Pt	Balance

31. A process according to Claim 23 in which the catalytic material comprises ruthenium.

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